Preparation of New Nitrogen-Bridged Heterocycles. XXIII.[1] Syntheses and Reactions of Pyrazolo[1,5-*a*]pyridine-2-thiols. (1)

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Some pyridinium 1-[[(2-substituted ethyl)thio]thiocarbonyl]aminides (4a—h) were prepared in moderate yields by the reactions of *N*-unsubstituted pyridinium aminides (2a—e) with carbon disulfide and ethyl acrylate (3a) or acrylonitrile (3b). The *S*-alkylations of these aminides 4a—h with bromoacetonitrile (5a) or ethyl bromoacetate (5b) at room temperature and the subsequent treatment of the resulting pyridinium salts with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and then with chloranil at 0 °C gave the corresponding 2-[(2-substituted ethyl)thio]pyrazolo[1,5-*a*]pyridine derivatives (6a—p) in 40—75% yields. The *β*-eliminations of the 2-substituents in these pyrazolo[1,5-*a*]pyridines 6a—p with potassium *tert*-butoxide in *N,N*-dimethylfomamide (DMF) proceeded smoothly to provide the title compounds, pyrazolo[1,5-*a*]pyridine-2-thiols (7a—j), in good yields along with the release of 3a, b.

Keywords pyridinium 1-(thiocarbonyl)aminide; 2-[(substituted ethyl)thio]pyrazolo[1,5-*a*]pyridine: pyrazolo[1,5-*a*]pyridine; pyrazolo[1,5-*a*]pyridine-2-thiols; *β*-elimination; deprotection

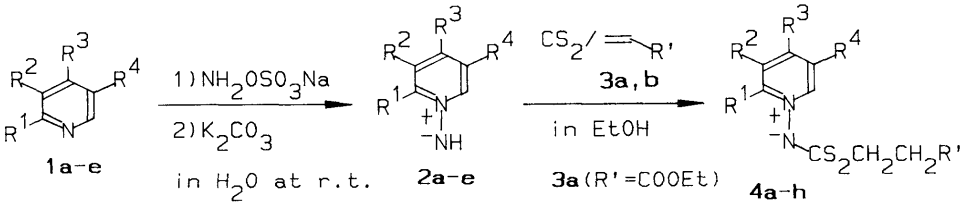
In our recent papers[2] we described a new synthetic approach to some 2-indolizinethiol derivatives which have been proved to be versatile intermediates for various polyfunctionalized indolizines and some thiophene-fused indolizines.[3] In particular, the main features of this method are the easy introduction of the protecting groups, 2-cyanoethyl and 2-(ethoxycarbonyl)ethyl groups, by means of the Michael addition, and the smooth deprotection by *β*-elimination reaction. Olefin syntheses by the *β*-eliminations of various substrates are very familiar,[4] but the use of 2-cyanoethyl and 2-ethoxycarbonylethyl groups as protecting groups for a mercapto function has scarcely been documented.[5] The success of this reaction sequence in an indolizine system prompted us to investigate a further extension to another heterocyclic system, pyrazolo[1,5-*a*]pyridine, since the corresponding pyrazolo[1,5-*a*]pyridine-2-thiols and their *S*-functionalized derivatives are synthetically and pharmaceutically interesting.[6] In this paper we wish to report the preparation and deprotection of some *S*-protected pyrazolo[1,5-*a*]pyridine derivatives.

Results and Discussion

Preparations of Pyridinium 1-Aminides (4a—h) Pyridinium 1-(thiocarbonyl)aminides (**4a—h**) having a (2-ethoxycarbonylethyl)thio or (2-cyanoethyl)thio group on the thiocarbonyl carbon were prepared in 33—49% yields by the reactions of freshly prepared pyridinium *N*-unsubstituted 1-aminides **2a—e**[7] with carbon disulfide and ethyl acrylate (**3a**) or acrylonitrile (**3b**) in ethanol (Chart 1). As has been proposed in connection with the preparations of similar types of pyridinium 1-methylides,[2] the formation of these aminides **4a—h** can be considered to proceed *via* the addition of carbon disulfide to the anionic nitrogen in the aminides **2a—e** followed by the Michael addition of the resulting pyridinium 1-(dithiocarboxy)aminides to the oleflnic compounds **3a, b**.

The presence of the *S*-protecting groups, 2-ethoxycarbonylethyl and 2-cyanoethyl groups, in these aminides **4a—h** was shown clearly by the characteristic absorption bands due to an ester carbonyl (1703—1720 cm^{-1}) or a cyano group (2239 or 2240 cm^{-1}) in the infrared (IR) spectra, and by four proton multiplet signals in the range of δ 2.5—3.6 attributable to the ethylene group in the proton nuclear magnetic resonance (^{1}H-NMR) spectra.

Preparations of *S*-Protected Pyrazolo[1,5-*a*]pyridines (6a—p) When pyridinium 1-aminides **4a—h** were treated with bromoacetonitrile (**5a**) in chloroform at room temperature for 3—6 d and the resulting pyridinium salts

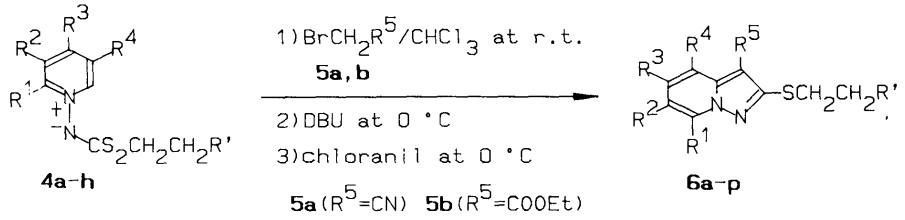


1,2	R^1	R^2	R^3	R^4
a	H	H	H	H
b	Me	H	H	H
c	H	H	Me	H
d	H	H	Et	H
e	H	Me	H	Me

4	R^1	R^2	R^3	R^4	R'
a	H	H	H	H	COOEt
b	Me	H	H	H	COOEt
c	H	H	Me	H	COOEt
d	H	H	Et	H	COOEt
e	H	Me	H	Me	COOEt

4	R^1	R^2	R^3	R^4	R'
f	H	H	H	H	CN
g	Me	H	H	H	CN
h	H	H	Me	H	CN

Chart 1



6	R^1	R^2	R^3	R^4	R^5	R'
a	H	H	H	H	CN	COOEt
b	Me	H	H	H	CN	COOEt
c	H	H	Me	H	CN	COOEt
d	H	H	Et	H	CN	COOEt
e	H	Me	H	Me	CN	COOEt
f	H	H	H	H	CN	CN
g	Me	H	H	H	CN	CN
h	H	H	Me	H	CN	CN

6	R^1	R^2	R^3	R^4	R^5	R'
i	H	H	H	H	COOEt	COOEt
j	Me	H	H	H	COOEt	COOEt
k	H	H	Me	H	COOEt	COOEt
l	H	H	Et	H	COOEt	COOEt
m	H	Me	H	Me	COOEt	COOEt
n	H	H	H	H	COOEt	CN
o	Me	H	H	H	COOEt	CN
p	H	H	Me	H	COOEt	CN

Chart 2

TABLE I. ^{1}H-NMR Spectral Data for 2-(Substituted Ethylthio)pyrazolo[1,5-*a*]pyridines

Compd. 6	δ ($CDCl_3$)[a] C-4	C-5		C-6	C-7	SCH_2CH_2		R'		R^5	
6a	7.67	7.44		6.64	8.49	2.85	3.50	1.28	4.19	—	
	brd	brt		dt	brd	brt	brt	t	q		
6b	7.2—7.7			6.79	2.75	2.89	3.49	1.24	4.15	—	
	m			brd	s	brt	brt	t	q		
6c	7.37	2.41		6.74	8.33	2.80	3.42	1.23	4.13	—	
	brs	s		dd	d	brt	brt	t	q		
6d	7.38	1.20	2.72	6.77	8.39	2.79	3.40	1.23	4.12	—	
	brs	t	q	dd	d	brt	brt	t	q		
6e	2.57	6.97		2.27	8.16	2.76	3.38	1.23	4.13	—	
	s	brs		s	brs	brt	brt	t	q		
6f	7.3—7.9			7.00	8.54	2.90	3.43	—		—	
	m			dt	brd	m	m				
6g	7.2—7.8			6.87	2.75	2.97	3.50	—		—	
	m			brd	s	m	m				
6h	7.42	2.45		6.81	8.37	2.89	3.39	—		—	
	brs	s		dd	d	m	m				
6i	8.05	7.35		6.83	8.44	2.86	3.43	1.26	4.11	1.40	4.32
	brd	brt		dt	brd	brt	brt	t	q	t	q
6j	7.98	7.32		6.73	2.74	3.10	3.52	1.26	4.18	1.44	4.38
	brd	q		brd	s	brt	brt	t	q	t	q
6k	7.79	2.38		6.64	8.31	2.84	3.39	1.25	4.12	1.37	4.32
	brs	s		dd	d	brt	brt	t	q	t	q
6l	7.83	1.26	2.82	6.69	8.34	2.64	3.42	1.26	4.13	1.41	4.32
	brs	t	q	dd	d	brt	brt	t	q	t	q
6m	2.58	6.92		2.21	8.09	2.83	3.37	1.24	4.11	1.36	4.30
	s	brs		s	brs	brt	brt	t	q	t	q
6n	8.03	7.39		6.82	8.42	2.85	3.38	—		1.38	4.31
	brd	brt		dt	brd	m	m			t	q
6o	7.94	7.31		6.74	2.73	3.00	3.51	—		1.44	4.34
	brd	q		brd	s	m	m			t	q
6p	7.79	2.38		6.71	8.30	2.91	3.34	—		1.38	4.32
	brs	s		dd	d	m	m			t	q

a) The coupling constants are as follows: $J_{4,5}=9.0$, $J_{5,6}=J_{6,7}=7.0$, $J_{4,6}=2.0$, $J_{ethylene}=ca.$ 7.0, and $J_{Et}=7.0$ Hz.

were allowed to react with DBU and then chloranil in an ice bath, the expected 2-[(2-ethoxycarbonylethyl)thio]-(**6a**—**e**) and 2-[(2-cyanoethyl)thio]pyrazolo[1,5-*a*]pyridine-3-carbonitriles (**6f**—**h**) were obtained in 40—69% yields. Similar reactions of the aminides **4a**—**h** with ethyl bromoacetate (**5b**), DBU, and chloranil gave the corresponding ethyl pyrazolo[1,5-*a*]pyridine-3-carboxylates (**6i**—**p**) in 50—75% yields, respectively (Chart 2).

The ^{1}H-NMR spectra (Table I) of these pyrazolo[1,5-*a*]pyridine derivatives **6a**—**p** showed characteristic proton signals due to the 2-substituents at δ 2.76—3.10 (2H) and δ 3.37—3.52 (2H) as broad triplets or multiplets (ethylene

group), and at δ near 1.25 (3H, t) and 4.15 (2H, q) (ethoxyl group), together with the signals of the skeletal protons (δ 6.64—8.54), the methyl groups (δ 2.21—2.75), and the ethyl groups (δ 1.20 or 1.26 and 2.72 or 2.82 (skeletal), and δ near 1.40 and 4.30 (ester)). The chemical shifts and signal patterns of the skeletal protons and methyl protons are grossly similar to those of pyrazolo[1,5-*a*]pyridines prepared previously by us[8] and by other investigators,[9] and the chemical shifts of ethylene groups are also almost the same as those of 2-[(2-substituted ethyl)thio]indolizines reported recently by us.[2] The IR spectra of compounds **6a**—**p** clearly exhibited the unique absorption bands supporting our proposed structures; for example, normal ester carbonyl bands are seen at 1718—1733 cm^{-1}, α, β-unsaturated ones at 1670—1688 cm^{-1}, normal cyano bands at 2238—2247 cm^{-1}, and α,β-unsaturated ones at 2208—2220 cm^{-1}. The elementary analyses of **6a**—**p** were also in good accord with their proposed compositions.

TABLE II. ^{1}H-NMR Spectral Data for Pyrazolo[1,5-*a*]pyridine-2-thiols

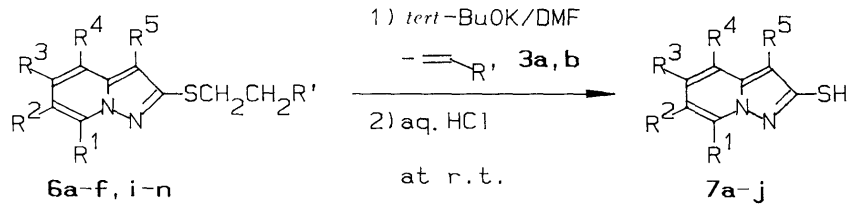
Compd. 7	δ ($CDCl_3$)[a] C-4	C-5		C-6	C-7	SH	R^5	
7a	7.2—7.9 m			6.96 dt	8.43 brd	3.64 brs	—	
7b	7.1—7.8 m			6.81 brd	2.75 s	3.75 brs	—	
7c	7.37 brs	2.43 s		6.76 dd	8.36 d	3.84 brs	—	
7d	7.38 brs	1.29 t	2.73 q	6.82 dd	8.37 d	3.79 brs	—	
7e	2.70 s	7.05 brs		2.36 s	8.13 brs	3.40 brs	—	
7f	8.03 brd	7.40 brt		6.86 dt	8.44 brd	5.48 brs	1.40 t	4.37 q
7g	7.95 brd	7.34 q		6.72 brd	2.72 s	5.08 brs	1.43 t	4.41 q
7h	7.77 brs	2.40 s		6.69 dd	8.33 d	5.28 brs	1.41 t	4.36 q
7i	7.77 brs	1.29 t	2.72 q	6.70 dd	8.30 d	5.86 brs	1.44 t	4.35 q
7j	2.65 s	6.90 brs		2.27 s	7.99 brs	5.35 brs	1.44 t	4.34 q

The coupling constants are as follows: $J_{4,5}=9.0$, $J_{5,6}=J_{6,7}=7.0$, $J_{4,6}=2.0$, and $J_{Et}=7.0$ Hz.

Preparations of Pyrazolo[1,5-*a*]pyridine-2-thiols(7a—j) According to the procedure reported earlier by us,[2] the reaction of 2-[(2-ethoxycarbonylethyl)thio]pyrazolo[1,5-*a*]pyridine-3-carbonitrile (**6a**) with potassium *tert*-butoxide in *N,N*-dimethylformamide (DMF) at room temperature for 2 h followed by the quenching of the reaction mixture with diluted hydrochloric acid gave the expected 2-mercaptopyrazolo[1,5-*a*]pyridine-3-carbonitrile (**7a**) as colorless crystals in 77% yield. The same compound **7a** was also obtained in 79% yield by the reaction of the 2-[(2-cyanoethyl]thio derivative **6f** with the same reagents. Similar reactions of *S*-protected pyrazolo[1,5-*a*]pyridines **6b**—**e**, **6i** and **6n**, and **6j**—**m** provided the corresponding pyrazolo[1,5-*a*]pyridine-2-thiol derivatives **7b**—**j** in 68—95% yields, respectively. In these reactions the smooth evolution of ethyl acrylate (**3a**) or acrylonitrile (**3b**) was not only confirmed by the characteristic odor but also detected by gas chromatographic monitoring of the reaction solutions of **6a**, **c**, **f**, **n** (Chart 3).

The structures of these 2-mercapto derivatives **7a**—**j** could be easily determined by confirming the disappearance of the protecting groups and the presence of the newly formed mercapto function in their ^{1}H-NMR spectra (Table II) and IR spectra; for example, the ^{1}H-NMR spectra did not show any significant proton signals due to the 2-ethoxycarbonylethyl or 2-cyanoethyl group but exhibited a distinct mercapto proton signal as a broad singlet at δ 3.64—3.84 (R^5 = CN) or 5.08—5.86 (R^5 = COOEt). In the IR spectra, the characteristic absorption bands attributable to the mercapto, the α, β-unsaturated cyano, and the α,β-unsaturated carbonyl groups appeared in the ranges of 2390—2595, 2211—2219, and 1662—1690 cm^{-1}, respectively.

In conclusion, some pyrazolo[1,5-*a*]pyridine-2-thiol derivatives **7a**—**j** which are inaccessible by other methods were prepared with ease by the reaction sequence using the combination of the Michael addition and β-elimination, and the utility of 2-ethoxycarbonylethyl and 2-cyanoethyl groups as protecting groups for a mercapto function has been proved.



7	react.(6)	R^1	R^2	R^3	R^4	R^5	7	react.(6)	R^1	R^2	R^3	R^4	R^5
a	a or f	H	H	H	H	CN	**f**	i or n	H	H	H	H	COOEt
b	b	Me	H	H	H	CN	**g**	j	Me	H	H	H	COOEt
c	c	H	H	Me	H	CN	**h**	k	H	H	Me	H	COOEt
d	d	H	H	Et	H	CN	**i**	l	H	H	Et	H	COOEt
e	e	H	Me	H	Me	CN	**j**	m	H	Me	H	Me	COOEt

Chart 3

Experimental

Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. The microanalyses were carried out on a Perkin–Elmer 240 elemental analyzer. The ^{1}H-NMR spectra were determined with a Varian EM360A spectrometer in deuteriochloroform with tetramethylsilane as an internal standard and the chemical shifts are expressed in δ values. The IR spectra were taken with a Hitachi 260-10 infrared spectrophotometer. The gas chromatography was performed with Shimadzu GS-4B gas chromatograph using a stainless steel column (3 mm × 2 m) packed with diethylene glycol–succinate polyester.

Preparations of Pyridinium 1-(Thiocarbonyl)aminides (4a—h). General Method A solution of hydroxylamine-*O*-sulfonic acid (11.1 g, 0.1 mol)[7] in 50 ml of water was neutralized with aqueous sodium hydroxide (4.0 g (0.1 mol) in 30 ml of water) in an ice bath. A pyridine derivative (0.15 mol) was added to the solution and the mixture was stirred at room temperature for 2—3 d. Anhydrous potassium carbonate (13.8 g, 0.1 mol) and then ethanol (200 ml) were added to the solution; the resulting suspension was stirred for an additional 0.5 h, and then filtered to remove insoluble substances. The filtrates were concentrated under reduced pressure and the residue was dissolved in ethanol (100 ml). The ethanolic solution was again filtered and the filtrate was allowed to react with carbon disulfide (10 g, 0.13 mol) and ethyl acrylate (**3a**, 10 g, 0.1 mol) or acrylonitrile (**3b**, 5.3 g, 0.1 mol) in a water bath (10 °C) for 2 h. The reaction mixture was concentrated under reduced pressure and the residue was separated by column chromatography (alumina) using chloroform as an eluent. After the removal of the solvent, the crude product was recrystallized from chloroform–ether to give the corresponding pyridinium 1-(thiocarbonyl)-aminides **4a—h**.

The results are listed in Table III together with the spectral and analytical data.

Preparations of *S*-Protected Pyrazolo[1,5-*a*]pyridines (6a—p). General Method A chloroform solution (30 ml) of a pyridinium 1-(thiocarbonyl)-aminide (**4**, 5 mmol) and bromoacetonitrile (**5a**, 0.60 g, 6 mmol) or ethyl bromoacetate (**5b**, 1.00 g, 6 mmol) was kept standing for 3—6 d until the aminide was no longer detectable by thin layer chromatographic monitoring. An additional 30 ml of chloroform was poured into the solution and the resulting solution of pyridinium salt was allowed to react with DBU (0.91 g, 6 mmol) for 10 min and then with chloranil (1.23 g, 5 mmol) in an ice bath for 6 h. The reaction mixture was concentrated under reduced pressure and the residue was separated by column chromatography (alumina) using chloroform as an eluent. Evaporation of the solvent followed by recrystallization of the crude compound afforded the corresponding 2-[(2-substituted ethyl)thio]pyrazolo[1,5-*a*]pyridine derivatives **6a—p**.

The results and some data are summarized in Tables I and IV.

Preparations of Pyrazolo[1,5-*a*]pyridine-2-thiols(7a—j). General Method Potassium *tert*-butoxide (0.168 g, 1.5 mmol) was added to a DMF solution (2 ml) of 2-[(2-ethoxycarbonylethyl)thio]- or 2[(2-cyanoethyl)thio]-pyrazolo[1,5-*a*]pyridine (**6**, 1 mmol), at room temperature; after sufficient stirring using a spatula, the resulting mixture was kept standing for an additional 2 h. The reaction solution was neutralized with dilute hydrochloric acid, and the precipitates separated were collected by filtration and washed twice with water (20 ml). The crude product was dissolved again in chloroform (30 ml) and freed from water by filtration through a phase separating filter paper. The filtrates were concentrated under reduced pressure and the residue was separated by column chromatography (alumina) using chloroform as an eluent. Evaporation of the solvent followed by recrystallization from ethanol gave the corresponding

Table III. Some Data for Pyridinium 1-Aminides

Compd. 4[a]	React. 1	React. 3	Yield (%)	mp (°C)	ν (KBr)	δ ($CDCl_3$) SCH_2CH_2R'	Formula	Analysis (%) Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
4a	**1a**	**3a**	44	94—95	1714, 975	2.5—3.4 m	$C_{11}H_{14}N_2O_2S_2$	48.87	5.22	10.36	48.75	5.10	10.60
4b	**1b**	**3a**	48	97—98	1719, 983	2.5—3.5 m	$C_{12}H_{16}N_2O_2S_2$	50.68	5.67	9.85	50.61	5.64	9.96
4c	**1c**	**3a**	40	110—111	1718, 977	2.5—3.5 m	$C_{12}H_{16}N_2O_2S_2$	50.68	5.67	9.85	50.48	5.67	10.04
4d	**1d**	**3a**	33	105—107	1720, 980	2.5—3.5 m	$C_{13}H_{18}N_2O_2S_2$	52.32	6.08	9.39	52.44	5.93	9.66
4e	**1e**	**3a**	49	104—106	1703, 980	2.5—3.5 m	$C_{13}H_{18}N_2O_2S_2$	52.32	6.08	9.39	52.20	6.00	9.60
4f	**1a**	**3b**	49	119—120	2240, 959	2.6—3.6 m	$C_9H_9N_3S_2$	48.41	4.06	18.82	48.21	4.06	19.01
4g	**1b**	**3b**	51	112—113	2239, 977	2.6—3.5 m	$C_{10}H_{11}N_3S_2$	50.61	4.67	17.70	50.58	4.56	17.84
4h	**1c**	**3b**	49	131—132	2240, 950	2.6—3.6 m	$C_{10}H_{11}N_3S_2$	50.61	4.67	17.70	50.55	4.58	17.85

a) Compounds **4a**, **b** were obtained as colorless needles, **4c**, **e**—**g** as colorless prisms, and **4d**, **h** as colorless flakes.

Table IV. Some Data for 2-(Substituted ethylthio)pyrazolo[1,5-*a*]pyridines

Compd. 6[a]	React. 4	React. 5	Yield (%)	mp (°C)	ν (KBr)	Formula	Analysis (%) Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
6a	**4a**	**5a**	51	80	2217, 1722	$C_{13}H_{13}N_3O_2S$	56.71	4.76	15.26	56.64	4.94	15.07
6b	**4b**	**5a**	53	104—105	2208, 1727	$C_{14}H_{15}N_3O_2S$	58.11	5.23	14.52	57.93	5.33	14.41
6c	**4c**	**5a**	60	93—94	2212, 1724	$C_{14}H_{15}N_3O_2S$	58.11	5.23	14.52	58.12	5.25	14.49
6d	**4d**	**5a**	69	57	2210, 1718	$C_{15}H_{17}N_3O_2S$	59.39	5.65	13.85	59.32	5.57	13.84
6e	**4e**	**5a**	67	92—93	2210, 1725	$C_{15}H_{17}N_3O_2S$	59.39	5.65	13.85	59.51	5.41	13.97
6f	**4f**	**5a**	42	125—127	2245, 2220	$C_{11}H_8N_4S$	57.88	3.53	24.54	57.76	3.60	24.24
6g	**4g**	**5a**	40	144—146	2246, 2212	$C_{12}H_{10}N_4S$	59.48	4.16	23.12	59.55	4.30	22.91
6h	**4h**	**5a**	50	125—127	2242, 2211	$C_{12}H_{10}N_4S$	59.48	4.16	23.12	59.38	4.02	23.28
6i	**4a**	**5b**	55	100—101	1725, 1685	$C_{15}H_{18}N_2O_4S$	55.89	5.63	8.69	55.70	5.63	8.66
6j	**4b**	**5b**	58	80—81	1730, 1686	$C_{16}H_{20}N_2O_4S$	57.13	5.99	8.33	57.11	6.07	8.27
6k	**4c**	**5b**	66	72—73	1733, 1688	$C_{16}H_{20}N_2O_4S$	57.13	5.99	8.33	56.98	6.02	8.26
6l	**4d**	**5b**	54	53—54	1725, 1688	$C_{17}H_{22}N_2O_4S$	58.27	6.33	7.99	58.55	6.35	8.12
6m	**4e**	**5b**	54	63—65	1721, 1690	$C_{17}H_{22}N_2O_4S$	58.27	6.33	7.99	58.11	6.15	8.10
6n	**4f**	**5b**	60	95—96	2247, 1690	$C_{13}H_{13}N_3O_2S$	56.71	4.76	15.26	56.94	4.78	15.01
6o	**4g**	**5b**	50	143—145	2238, 1670	$C_{14}H_{15}N_3O_2S$	58.11	5.23	14.52	58.21	5.14	14.51
6p	**4h**	**5b**	75	117—118	2239, 1688	$C_{14}H_{15}N_2O_2S$	58.11	5.23	14.52	58.20	5.35	14.30

a) Compounds **6a**—**f**, **i**, **k**—**n**, **p** were obtained as colorless needles, **6g**, **h**, **j** as colorless flakes, and **6o** as colorless prisms.

TABLE V. Some Data for Pyrazolo[1,5-*a*]pyridine-2-thiols

Compd. 7[a)]	React. 6	Yield (%)	mp (°C)	*v* (KBr)	Formula	Analysis (%) Calcd			Found		
						C	H	N	C	H	N
7a	**6a**	77	134—136	2390, 2213	$C_8H_5N_3S$	54.84	2.88	23.98	55.02	2.88	23.79
	6f	69									
7b	**6b**	95	151—153	2471, 2211	$C_9H_7N_3S$	57.12	3.73	22.21	57.44	3.79	21.83
7c	**6c**	88	162—164	2430, 2213	$C_9H_7N_3S$	57.12	3.73	22.21	57.32	3.77	21.97
7d	**6d**	85	155—157	2520, 2219	$C_{10}H_9N_3S$	59.09	4.46	20.67	59.39	4.23	20.66
7e	**6e**	87	205—208	2440, 2217	$C_{10}H_9N_3S$	59.09	4.46	20.67	58.95	4.51	20.51
7f	**6i**	68	101—103	2450, 1664	$C_{10}H_{10}N_2O_2S$	54.04	4.54	12.60	54.28	4.65	12.45
	6n	71									
7g	**6j**	60	89—91	2500, 1663	$C_{11}H_{12}N_2O_2S$	55.91	5.12	11.86	55.99	5.30	12.01
7h	**6k**	83	84—86	2485, 1663	$C_{11}H_{12}N_2O_2S$	55.91	5.12	11.86	55.92	4.99	11.97
7i	**6l**	91	75—77	2480, 1662	$C_{12}H_{14}N_2O_2S$	57.58	5.64	11.19	57.80	5.76	10.89
7j	**6m**	77	103—105	2595, 1690	$C_{12}H_{14}N_2O_2S$	57.58	5.64	11.19	57.36	5.69	11.45

a) All compounds were obtained as colorless needles.

pyrazolo[1,5-*a*]pyridine-2-thiol derivatives **7a**—**j** as colorless needles.

In the reactions of **6a**, **c**, **f**, **n** the generation of ethyl acrylate (**3a**) or acrylonitrile (**3b**) was confirmed by gas chromatographic monitoring.

The results and some data are shown in Tables III and V.

References and Notes

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